Naturally occurring inorganic nanoparticles: General assessment and a global budget for one of Earth's last unexplored major geochemical components

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Naturally occurring inorganic nanoparticles have been one of the principal catalytic components of Earth throughout its history. Yet these ubiquitous materials have largely escaped our close scrutiny until very recently. They are illusive and difficult to study. They have properties that change significantly with their exact size, shape, aggregation state, and surrounding environment. It has not even been clear how they accumulate, disperse, and move around the planet, nor even for sure what their major sources and sinks are. In this project, we derive a global budget for naturally occurring inorganic nanoparticles, assessing the sources and sinks for there materials, as well as the fluxes between these compartments (atmosphere, continents, continental shelves, and open oceans). Although this worldwide natural nanomaterial budget has a great amount of uncertainty because of limited available observations and data, it still should be a valuable guide as geoscientists attempt to better understand this poorly understood, yet fundamentally important driver of many significant Earth processes and functions. In addition, these kinds of budgets provide a basis for fundamental understanding such as residence and transfer times between compartments.

Specific findings include the following: 1) The primary producer of Earth's inorganic nanoparticles is soil through terrestrial weathering processes; 2) rivers, and to a lesser extent glaciers, bring 0.1% to 0.01% of the Earth's continental nanomaterial reservoir to the continental edge/ocean margins each year; 3) only about 1.5% of this material makes it to the deep oceans due to aggregation and settling in saline ocean margins; and 4) the airborne and waterborne inputs of nanominerals and mineral nanoparticles to the open oceans are very similar.

Palaeotemperature estimation by tandem $\delta^{18}O$ measurement of calcium carbonate and gypsum hydration water

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A fundamental problem in oxygen isotope palaeothermometry is the carbonate mineral-water temperature equation is often under constrained. Both the oxygen isotope composition of the carbonate mineral and water from which it precipitated must be known to calculate temperature. Gypsum ($CaSO_4 \cdot 2H_2O$) is a hydrated mineral containing 20.9% water by weight that records the oxygen and hydrogen isotopic of the water from which it formed. If (i) isotopic equilibrium is achieved between the mother water and hydration water; (ii) the fractionation factors are known and temperature independent, and (iii) no exchange has occurred between environmental water and hydration water after deposition, then palaeotemperature can be calculated by measuring oxygen isotopes of co-occurring gypsum hydration water and biogenic carbonate. We developed a precise and accurate method for the simultaneous measurement of $\delta^{18}O$ and δD of gypsum hydration water by cavity ringdown spectroscopy using a Picarro water isotope analyzer. The fractionation factors between gypsum hydration water and mother water were re-determined to be $\alpha_{18O} = 1.004$ and $\alpha_D = 0.981$ and found to be temperature independent between 12 and 40°C, in excellent agreement with previous studies. Three paired measurements of 1200-yr old gypsum and carbonate from Lake Chichancanab, Mexico, yielded a temperature of 25°C (range 23 to 27 °C), which is equal to mean annual temperature (MAT) today. Twenty paired measurements of ostracods and gypsum hydration water samples from Late Peten-Itza, Guatemala, yielded a mean temperature of ~19°C (range 16 to 22 °C) for the Late Glacial period (18 to 10 ka), which is 6 to 7°C cooler than MAT today (~25 to 26°C). When isotope values of gypsum hydration waters from both lakes are corrected for fractionation, the $\delta^{18}O$ and δD of the palaeo-lake water fall on a projection of the modern evaporative line for the region with slope of ~5, suggesting the crystal water preserves the isotopic signal of the lake water, and has not undergone isotopic exchange with sediment pore water. The method is promising for deconvolving $\delta^{18}O$ of calcite into its temperature and $\delta^{18}O_{water}$ components.